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# Synthesis and characterization of alternating poly(amide urethane)s from $\epsilon$ -caprolactone, diamines and diphenyl carbonate

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## Abstract

The synthesis of alternating poly(amide urethane)s **5a–d** was performed in three steps using  $\epsilon$ -caprolactone, diamines, and diphenyl carbonate as starting materials. The microstructure and nature of the end groups of the poly(amide urethane)s were determined by means of <sup>1</sup>H NMR spectroscopy, which reveals an alternating sequence of amide and urethane linkages in a linear chain with hydroxy and phenyl urethane end groups. The molecular weight and polydispersity of the polymers obtained ( $5700 < \bar{M}_n < 7900$ ,  $1.25 < \bar{M}_w/\bar{M}_n < 1.38$ ) were determined by means of gel permeation chromatography. The thermal properties determined by means of DSC show that the poly(amide urethane)s **5a–d** are semicrystalline materials having one or two endothermic transitions similar to the poly(amide urethane)s **10a–d** prepared from  $\epsilon$ -caprolactam, amino alcohols, and diphenyl carbonate. Thermogravimetric analysis of poly(amide urethane)s **5a–b** shows a single step decomposition, while poly(amide urethane)s **10a–c** decompose in two steps indicating that different degradation mechanisms are operating. © 2004 Elsevier Ltd. All rights reserved.

**Keywords:** Polycondensation; Poly(amide urethane)s; Structure/property relation

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## 1. Introduction

There has been recent interest in using end functionalized low molecular weight prepolymers for the preparation of biodegradable networks [1–3] and coating materials [4]. Polymers and copolymers that contain  $\epsilon$ -caprolactone moieties are widely used for medical application, biodegradable sutures, tissue engineering, and artificial skin [5–7]. From the point of view of materials which might be of interest for the manufacture of powder coatings, we have already described the synthesis of alternating poly(amide urethane)s employing  $\epsilon$ -caprolactam, amino alcohols, and diphenyl carbonate or ethylene carbonate as carbonic acid esters in previous papers [8,9]. Furthermore, we prepared poly(amide urea)s and poly(amide urethane urethane)s from

$\epsilon$ -caprolactam, diamines, and diphenyl carbonate or ethylene carbonate [10]. We focused our attention on these carbonic acid esters which are substitutes for phosgene, and can become milestones to promote green chemistry. Ethylene carbonate is obtained from ethylene oxide and carbon dioxide [11], while diphenyl carbonate can be obtained from phenol and carbon monoxide [12] or urea [11].

In this communication, we present an alternating method for the synthesis of poly(amide urethane)s using  $\epsilon$ -caprolactone, diamines and diphenyl carbonate which are structural isomers of poly(amide urethane)s employing  $\epsilon$ -caprolactam, amino alcohols, and diphenyl carbonate as starting materials. Both series of polymers obtained have alternating amide and urethane linkages and were obtained without using isocyanates or phosgene. The final product shall be of low molecular weight with well defined end groups suitable as building blocks for more complex polymer architectures.

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Table 1

Yield and characteristic chemical shifts ( $^1\text{H}$  and  $^{13}\text{C}$  NMR) of  $\alpha$ -hydroxy- $\omega$ -amino amides **3a–d**

No.	<i>t</i> (h)	Yield (%)	Characteristic chemical shifts (DMSO- $d_6$ ): ( $\delta$ , ppm)					
			$\text{CH}_2\text{OH}$	$\text{CH}_2\text{--CO}$	$\text{CH}_2\text{--CO}$	$\text{CH}_2\text{--NH}$	$\text{CH}_2\text{--NH}$	$\text{CH}_2\text{NH}_2$
<b>3a</b>	25	84	3.34	2.04	–	3.03	7.75	2.51
			60.52	35.44	172.07	41.34	–	42.17
<b>3b</b>	20	93	3.37	2.03	–	3.06	7.78	2.50
			60.52	35.47	172.45	35.96	–	39.00
<b>3c</b>	24	90	3.36	2.03	–	2.97	7.79	2.50
			60.51	35.44	172.25	38.25	–	41.26
<b>3d</b>	47	75	3.36	2.03	–	3.01	7.74	2.50
			60.53	35.43	171.78	38.32	–	41.50

According to the NMR analysis the monomers are pure.

## 2. Experimental part

### 2.1. Materials

Starting materials and reagents used for the monomer synthesis and polymer synthesis were of high purity.  $\epsilon$ -Caprolactone (Acros Organics), 1,2-diaminoethane (BASF), 1,3-diaminopropane (BASF), 1,4-diaminobutane (67.5 wt% in water, DSM), 1,5-diaminopentane (Acros Organics), diphenyl carbonate (Fluka), dibutyldimethoxytin ( $\text{Bu}_2\text{Sn}(\text{OCH}_3)_2$ , Aldrich), tetrahydrofuran, formic acid, diethyl ether, dichloromethane and methanol were used as received.

### 2.2. Measurements

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer at 300 and 75 MHz, respectively. Deuterated trifluoroacetic acid (TFA- $d$ ) and dimethylsulfoxide (DMSO- $d_6$ ) were used as solvents, and tetramethylsilane (TMS) served as an internal standard.

Gel permeation chromatography (GPC) analyses were carried out using a high pressure liquid chromatography pump (Bischoff HPLC pump 2200) and a refractive index detector (Waters 410). The eluting solvent was  $N,N$ -dimethylacetamide (DMAc) with 2.44 g  $\text{L}^{-1}$  LiCl with a

flow rate of 0.8  $\text{mL min}^{-1}$ . Four columns with MZ-DVB gel were applied: length of each column 300 mm, diameter 8 mm, diameter of gel particles 5  $\mu\text{m}$ , nominal pore widths 100, 100,  $10^3$ , and  $10^4$  Å. Calibration with polystyrene standards was used for the estimation of molecular weights and polydispersities.

Thermogravimetric analyses (TGA) were performed on a TG 209 with a TA-System-Controller TASC 414/2 from Netzsch. The measurements were performed in a nitrogen atmosphere with a heating rate of 10  $\text{K min}^{-1}$ .

Differential scanning calorimetric (DSC) analyses were performed on a Netzsch DSC 204 in a nitrogen atmosphere with a heating and cooling rate of 10  $\text{K min}^{-1}$ . Calibration was achieved using indium standard samples.

### 2.3. Syntheses

#### 2.3.1. Preparation of $\alpha$ -hydroxy- $\omega$ -amino amide **3b**

$\epsilon$ -Caprolactone **1** (10 g, 87.7 mmol) and 1,3-diaminopropane **2b** (32.54 g, 439.7 mmol) were dissolved in THF (**1** in 10 mL, **2b** in 35 mL). The solution of  $\epsilon$ -caprolactone was added dropwise to the solution of 1,3-diaminopropane, and the mixture was stirred for 20 h at room temperature. THF and 1,3-diaminopropane were removed by distillation.

The same procedure was followed to prepare **3a–d**. The synthetic details and NMR data of  $\alpha$ -hydroxy- $\omega$ -amino amides **3a–d** are given in Table 1.

Table 2

Yield and characteristic chemical shifts ( $^1\text{H}$  and  $^{13}\text{C}$  NMR) of  $\alpha$ -hydroxy- $\omega$ - $O$ -phenyl urethane amides **4a–d**

No.	<i>t</i> (h)	Yield (%)	Characteristic chemical shifts (DMSO- $d_6$ ): ( $\delta$ , ppm)					
			$\text{CH}_2\text{OH}$	$\text{CH}_2\text{--CO}$	$\text{CH}_2\text{--CO}$	$\text{CH}_2\text{--NH}$	$\text{CH}_2\text{--NH}$	$\text{CH}_2\text{NHCO--OPh}$
<b>4a</b>	38	85	3.38	2.06	–	3.15	7.89	3.11
			60.53	35.44	172.33	38.18	–	40.22
<b>4b</b>	24	84	3.39	2.06	–	3.08	7.81	3.06
			60.98	35.88	172.55	36.46	–	38.66
<b>4c</b>	36	87	3.37	2.04	–	3.04	7.76	3.04
			60.98	35.88	172.36	38.44	–	40.53
<b>4d</b>	38	71	3.37	2.04	–	3.05	7.74	3.01
			60.54	35.43	171.83	38.21	–	40.24

According to the NMR analysis the monomers are pure.

Table 3  
Yield and  $^1\text{H}$  NMR data of poly(amide urethane)s **5a–d**

No.	$t$ (h)	Yield (%)	Characteristic chemical shifts (DMSO- $d_6$ ): ( $\delta$ , ppm)					
			$\text{CH}_2\text{--O}$	$\text{CH}_2\text{--CO}$	$\text{CH}_2\text{--NH}$	$\text{CH}_2\text{--NH}$	$\text{CH}_2\text{NHCOO}$	$\text{NHCOO}$
<b>5a</b>	$1^n + 4^r$	82	3.89	2.03	3.03	7.81	3.03	7.07
<b>5b</b>	$1^n + 4^r$	92	3.90	2.04	3.02	7.76	2.96	7.08
<b>5c</b>	$1^n + 4^r$	88	3.89	2.02	2.99	7.74	2.99	7.07
<b>5d</b>	$1^n + 4^r$	88	3.88	2.03	2.98	7.73	2.98	7.02

$^n$  at normal pressure,  $^r$  at reduced pressure ( $p = 10^{-2}$  mbar).

### 2.3.2. Preparation of $\alpha$ -hydroxy- $\omega$ -O-phenyl urethane amide **4b**

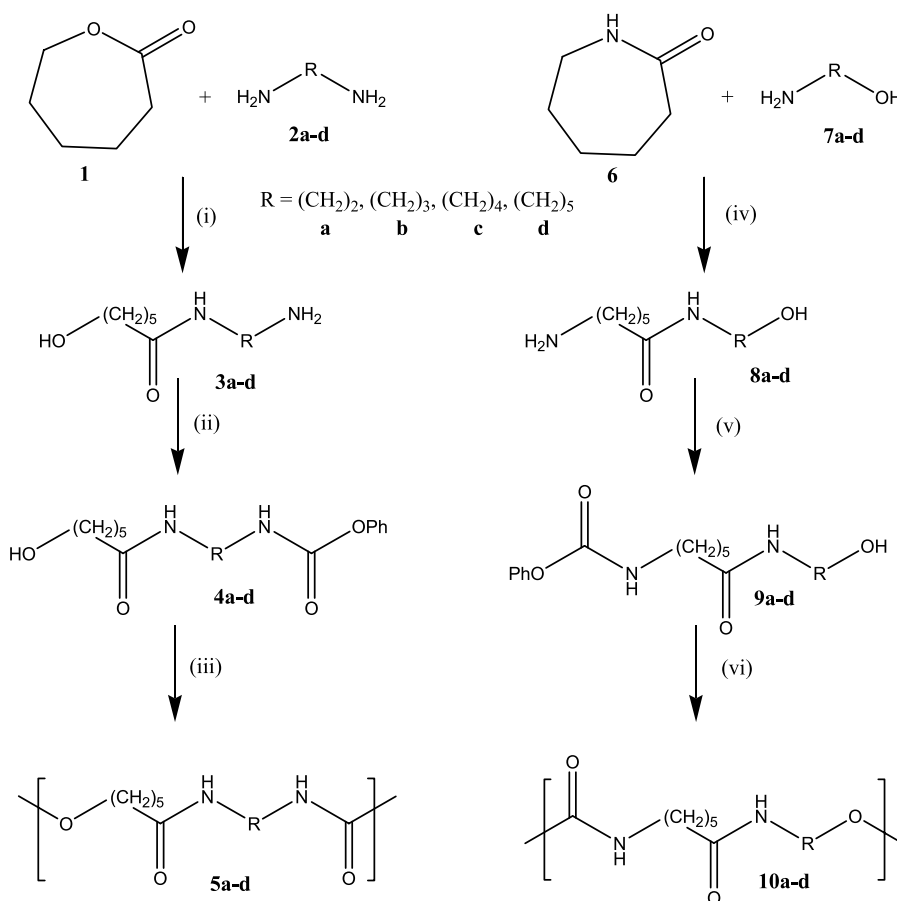
$\alpha$ -Hydroxy- $\omega$ -amino amide **3b** (10 g, 49.50 mmol) and diphenyl carbonate (13.24 g, 61.88 mmol) were reacted in the mixture of  $\text{CH}_2\text{Cl}_2$  (170 mL) and  $\text{CH}_3\text{OH}$  (20 mL) at room temperature for 24 h. 60–65% of the solvent were evaporated followed by precipitation into diethyl ether. The product was isolated by filtration and dried at  $50^\circ\text{C}$  under reduced pressure.

The same procedure was adopted to synthesize **4a–d**.

The synthetic details and NMR data of  $\alpha$ -hydroxy- $\omega$ -O-phenyl urethane amides **4a–d** are given in Table 2.

### 2.3.3. Preparation of alternating poly(amide urethane) **5b**

$\alpha$ -Hydroxy- $\omega$ -O-phenyl urethane amide **4b** (1.09 g, 3.538 mmol) was treated with  $\text{Bu}_2\text{Sn}(\text{OCH}_3)_2$  (5 wt%) at  $120^\circ\text{C}$ . The polycondensation was performed for 1 h at normal pressure and for 4 h at reduced pressure. For purification, the crude product was dissolved in  $\text{HCOOH}$  (5 mL) followed by precipitation into diethyl ether. The



Scheme 1. Synthesis of alternating poly(amide urethane)s; (i) **1/2a–d** = 1/5,  $T = \text{r.t.}$ ,  $t = 20\text{--}47$  h; (ii) diphenyl carbonate/**3a–d** = 1.25/1,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{OH}$  (10%),  $T = \text{r.t.}$ ,  $t = 24\text{--}38$  h; (iii) **4a–d**, 5 wt%  $\text{Bu}_2\text{Sn}(\text{OCH}_3)_2$ ,  $T = 120^\circ\text{C}$ ,  $t = 1$  h at normal pressure and  $t = 4$  h at reduced pressure ( $10^{-2}$  mbar); (iv) **6/7a–d** = 1/5,  $\text{H}_2\text{O}$ ,  $T = 200^\circ\text{C}$  in autoclave,  $t = 23\text{--}30$  h; (v) diphenyl carbonate/**8a–d** = 1/1–1.5/1,  $\text{CH}_2\text{Cl}_2$ ,  $\text{r.t.}$ ,  $t = 24\text{--}70$  h; (vi) **9a–d**, 5 wt%  $\text{Bu}_2\text{Sn}(\text{OCH}_3)_2$ ,  $T = 120^\circ\text{C}$ ,  $t = 1$  h at normal pressure and  $t = 3\text{--}6$  h at reduced pressure ( $10^{-2}$  mbar).

Table 4  
Characteristics of poly(amide urethane)s **5a–d**

Polymer	<i>t</i> (h)	Yield (%)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
<b>5a</b>	1 <sup>n</sup> + 4 <sup>r</sup>	82	7900	10,900	1.38
<b>5b</b>	1 <sup>n</sup> + 4 <sup>r</sup>	92	7700	9700	1.25
<b>5c</b>	1 <sup>n</sup> + 4 <sup>r</sup>	88	6900	9000	1.30
<b>5d</b>	1 <sup>n</sup> + 4 <sup>r</sup>	88	5700	7200	1.26

<sup>n</sup>at normal pressure, <sup>r</sup>at reduced pressure ( $p=10^{-2}$  mbar).

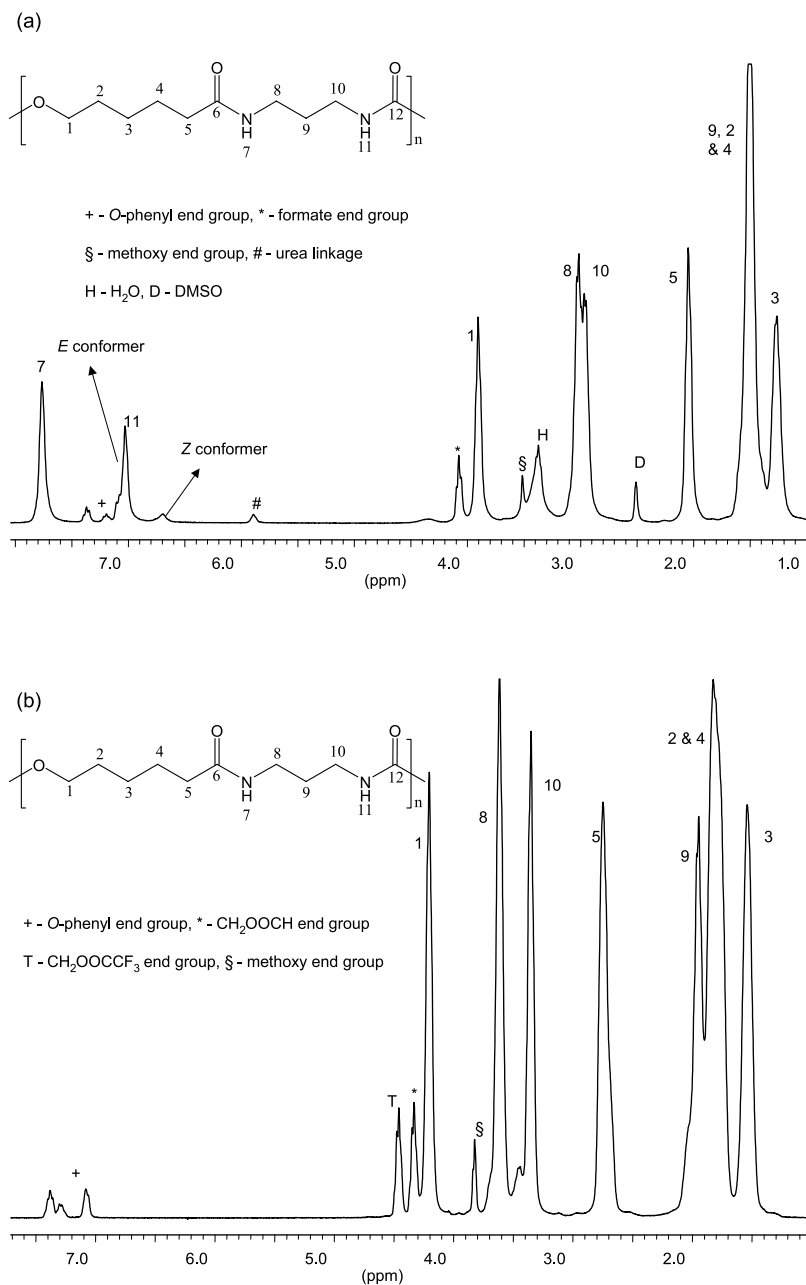
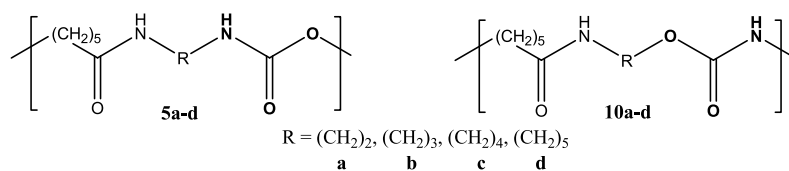


Fig. 1. <sup>1</sup>H NMR spectra of poly(amide urethane) **5b** in (a) DMSO-*d*<sub>6</sub> and (b) TFA-*d*.

Scheme 2. Poly(amide urethane)s **5a–d** and **10a–d**: structural isomers.

product was isolated by decantation and drying at 50 °C under reduced pressure.

The same procedure was adopted to synthesize poly(amide urethane)s **5a–d**. The yield and NMR data of poly(amide urethane)s **5a–d** are given in Table 3.

#### 2.3.4. Preparation of poly(amide urethane)s **10a–d**

The synthesis of poly(amide urethane)s using  $\epsilon$ -caprolactam and amino alcohols with diphenyl carbonate was reported in a previous paper, and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra in DMSO- $d_6$  and TFA- $d$  were in accord with the proposed structures [8].

### 3. Results and discussion

In previous papers [8–10], the successful synthesis of alternating poly(amide urethane)s, poly(amide urea)s, and poly(amide urethane urethane)s from  $\epsilon$ -caprolactam, amino alcohols or diamines, and diphenyl carbonate or ethylene carbonate was reported including their thermal properties. In this paper, we focus on a different route to synthesize poly(amide urethane)s comprising alternating amide and urethane linkages.

The synthesis of alternating poly(amide urethane)s **5a–d** was performed in three steps (Scheme 1). In the first step the diamines **2a–d** react with  $\epsilon$ -caprolactone **1** inducing ring-opening in a selective manner and resulting in the  $\alpha$ -hydroxy- $\omega$ -amino amides **3a–d**. In the second step the  $\alpha$ -hydroxy- $\omega$ -amino amides **3a–d** react with diphenyl carbonate selectively to give  $\alpha$ -hydroxy- $\omega$ -*O*-phenyl urethane amides **4a–d**. Finally,  $\alpha$ -hydroxy- $\omega$ -*O*-phenyl urethane amides **4a–d** are converted into the corresponding poly(amide urethane)s **5a–d** via polycondensation in bulk.

The  $\alpha$ -hydroxy- $\omega$ -amino amides were obtained by aminolysis of  $\epsilon$ -caprolactone with excess of diamine to prevent the reaction of both amine groups with  $\epsilon$ -caprolactone. It should be also mentioned that no oligomerization of  $\epsilon$ -caprolactone was observed under the reaction conditions. For the preparation of the  $\alpha$ -hydroxy- $\omega$ -*O*-phenyl urethane amides **4a–d**, the  $\alpha$ -hydroxy- $\omega$ -amino amides **3a–d** were treated with diphenyl carbonate in a mixture of methylene chloride and methanol as solvents at room temperature. Under these conditions only the amino groups react with diphenyl carbonate, not the hydroxy groups. The  $\alpha$ -hydroxy- $\omega$ -*O*-phenyl urethane amides **4a–d** were obtained in high purity and were used as starting material for the polycondensation. The polycondensation

was performed at 120 °C in the presence of  $\text{Bu}_2\text{Sn}(\text{OCH}_3)_2$  (5 wt%) as the catalyst. This temperature was found to be an optimum for the polycondensation of  $\alpha$ -hydroxy- $\omega$ -*O*-phenyl urethane amides **9a–d** [8]. The reaction conditions, number average molecular weight, polydispersity, and yield of the poly(amide urethane)s obtained are given in Table 4.

The  $^1\text{H}$  NMR spectrum of **3b** in DMSO- $d_6$  shows characteristic resonance lines at  $\delta=7.78$ , 3.50, and 2.50 ppm which were assigned to the protons of the amide linkage,  $\text{CH}_2\text{OH}$  and  $\text{CH}_2\text{NH}_2$ , respectively, and confirms the formation of the expected product.

The  $^1\text{H}$  NMR spectrum of **4b** clearly presents characteristic signals at  $\delta=7.00$  and 7.00–7.50 ppm for the protons of the newly formed phenyl urethane linkage. The disappearance of the  $\text{CH}_2\text{NH}_2$  signal at  $\delta=2.50$  ppm proves that conversion was complete.

The  $^1\text{H}$  NMR spectra in DMSO- $d_6$  and TFA- $d$  of the poly(amide urethane) **5b** (Fig. 1) show resonance signals for each methylene group. In DMSO- $d_6$  the resonance lines at  $\delta=7.00$ –7.10 and 7.70–7.90 ppm were assigned to the protons of the urethane and amide linkages, respectively. It has to be mentioned that for urethane protons two resonance lines ( $\delta=7.08$  and 6.72 ppm) with an intensity ratio of 9:1 corresponding to *E* and *Z* conformers are observed. The same observation was made by Neffgen et al. [13] and Rokicki et al. [14] In TFA- $d$ , the resonance lines of the protons of the amide and urethane linkages cannot be observed due to the fast exchange with deuterium of the solvent. The characteristic chemical shifts of the methylene protons adjacent to the functional groups are given in the experimental part.

Poly(amide urethane)s are expected to contain two end groups, i.e. *O*-phenyl urethane and  $\text{CH}_2\text{OH}$ . The *O*-phenyl urethane end group is observed in the range of  $\delta=7.00$ –7.50 ppm by means of  $^1\text{H}$  NMR spectroscopy in DMSO- $d_6$  as well as in TFA- $d$ . With respect to the  $\text{CH}_2\text{OH}$  end groups, a resonance signal of low intensity is observed in DMSO- $d_6$  at  $\delta=4.10$  ppm belonging to a formate end group. A formate end group is the result of the work up, because the purified product was obtained by precipitation of a solution in formic acid into diethyl ether. In formic acid, the  $\text{CH}_2\text{OH}$  end group converts into a  $\text{CH}_2\text{O}-\text{CH}=\text{O}$  group. On the other hand, in TFA- $d$ , additional resonance signals are observed at  $\delta=4.40$  and 4.55 ppm belonging to  $\text{CH}_2\text{O}-\text{CH}=\text{O}$  and  $\text{CH}_2\text{O}-\text{COCF}_3$  end groups. The formation  $\text{CH}_2\text{O}-\text{COCF}_3$  is the result of a transesterification with the NMR solvent  $\text{CF}_3\text{COOD}$ .

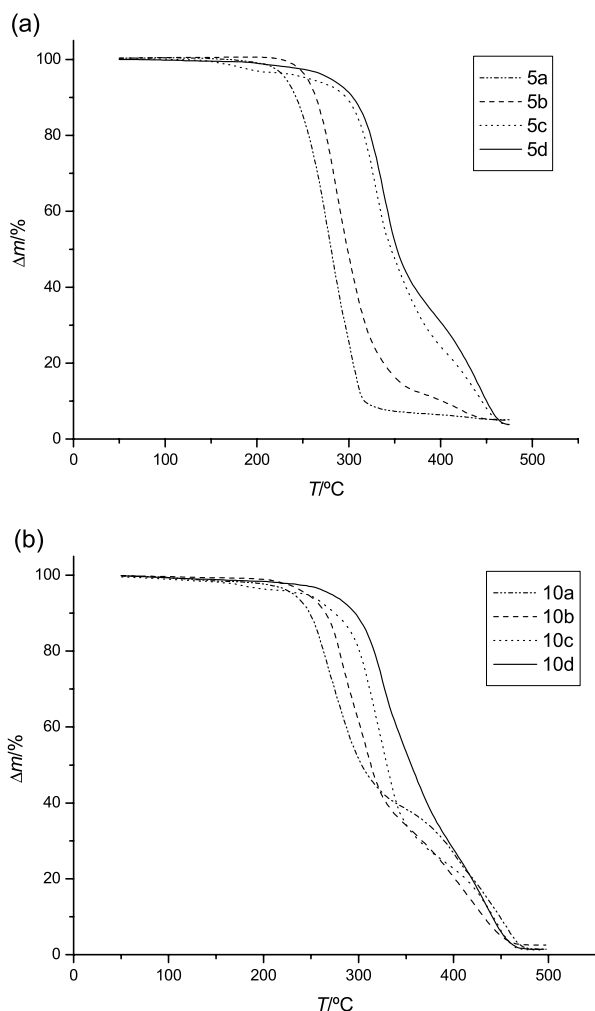


Fig. 2. TGA of the poly(amide urethane)s: (a) poly(amide urethane)s **5a–d** obtained via polycondensation of  $\alpha$ -hydroxy- $\omega$ -*O*-phenyl urethane amides **4a–d** at 120 °C; (b) poly(amide urethane)s **10a–d** obtained via polycondensation of  $\alpha$ -hydroxy- $\omega$ -*O*-phenyl urethane amides **9a–d** at 120 °C.

A resonance signal with small intensity was observed at  $\delta=5.75$  ppm attributed to protons of a urea linkages as was observed in the series of poly(amide urethane)s obtained from  $\epsilon$ -caprolactam, amino alcohols, and diphenyl carbonate [8] or ethylene carbonate [9]. These defects in the

microstructure, however, are below 5 mol%. As will be shown later in Section 3.1 the formation of urea linkages is the result of  $\epsilon$ -caprolactone elimination from the polymer chain.

In the  $^1\text{H}$  NMR spectrum of poly(amide urethane)s, a resonance line at  $\delta=3.45$  ppm in  $\text{DMSO}-d_6$  and  $\delta=3.85$  ppm in  $\text{TFA}-d$  was observed, which indicates the presence of an additional  $O\text{--CH}_3$  end group. The formation of the  $O\text{--CH}_3$  end group will be described in a forthcoming communication [15].

A comparison of the structural features of the repeating units of poly(amide urethane)s **5a–d** and of the poly(amide urethane)s **10a–d** [8] clearly reveals that these are structural isomers. In the series of poly(amide urethane)s **5a–d** and **10a–d** the oxygen and nitrogen atoms of the urethane function are interchanged (Scheme 2).

### 3.1. Thermal properties of poly(amide urethane)s **5a–d** and **10a–d**

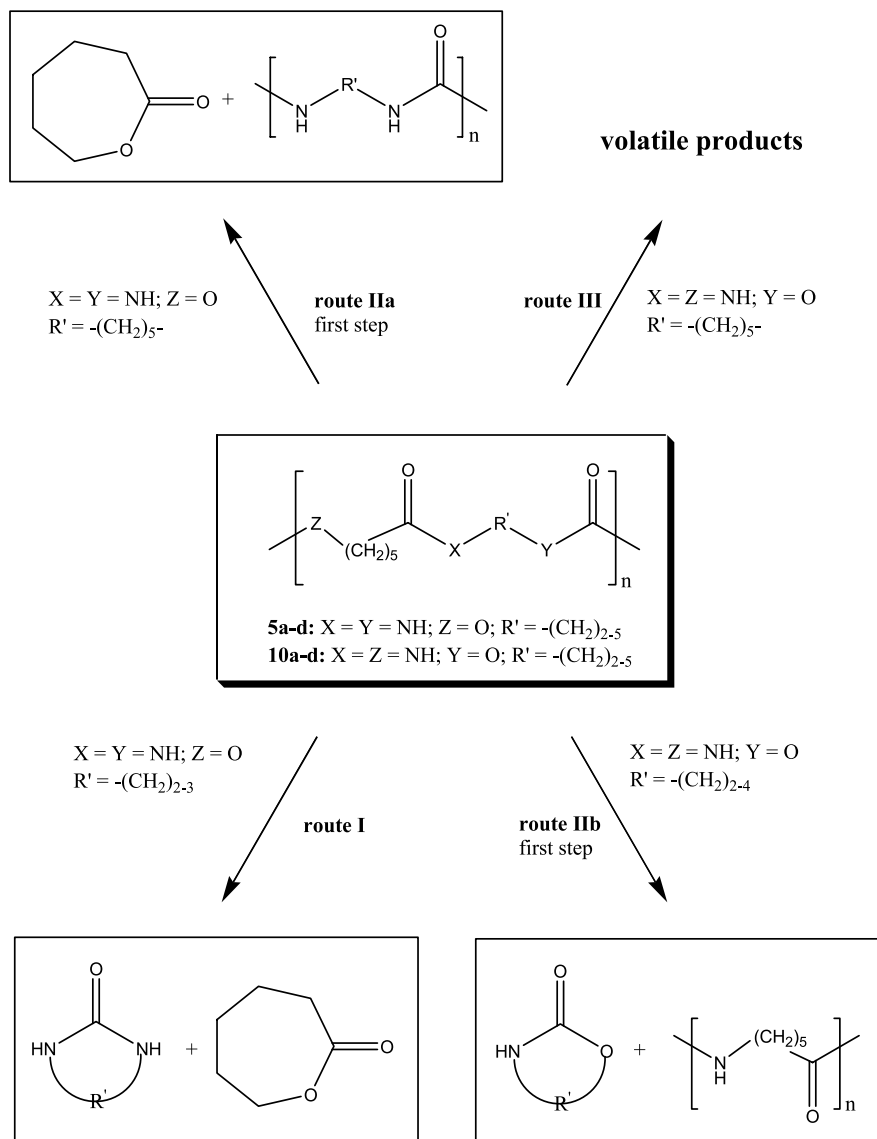
The thermogravimetric analyses of the poly(amide urethane)s **5a–d** and **10a–d** reveal a dependence of the degradation behavior on the chemical structure of the polymers (Fig. 2). The temperature for the maximum degradation rate as well as the temperatures for 5, 10, and 50% weight loss increase with increasing number of methylene groups. In the series of poly(amide urethane)s **5a–d**, polymers with 1,2-diaminoethane and 1,3-diaminopropane in the repeating unit (**5a,b**) clearly show a one-step degradation indicating that both building blocks form volatile products at the same time. Polymers **5c** and **5d** with 1,4-diaminobutane and 1,5-diaminopentane in the repeating unit show a degradation in two steps which is more pronounced in the case of **5d**. It is postulated that poly(amide urethane) **5a** and **5b** decompose by a zip reaction, with simultaneous formation of cyclic urea and  $\epsilon$ -caprolactone (Scheme 3, route I). They are removed from the crucible as volatiles in the temperature range of 250–300 °C. The decomposition of polymer **5c** and **5d** proceeds in two steps, first  $\epsilon$ -caprolactone and a polyurea is obtained—but no 7 and 8 membered cyclic urea is produced—and at higher temperatures the polyurea decomposes, too (Scheme 3, route IIa).

Table 5

Temperature of poly(amide urethane)s **5a–d** and **10a–d** at different weight loss measured by means of TGA

Polymer	$\bar{M}_n$ GPC	$T$ (°C) at 5% weight loss	$T$ (°C) at 10% weight loss	$T$ (°C) at 50% weight loss	$T$ (°C) at 90% weight loss
<b>5a</b>	7900	231	243	281	317
<b>5b</b>	7700	255	264	299	402
<b>5c</b>	6900	256	297	346	445
<b>5d</b>	5700	279	305	353	450
<b>10a</b>	8900	232	249	303	449
<b>10b</b>	7400	245	265	313	432
<b>10c</b>	8300	245	275	329	442
<b>10d</b>	11,500	271	295	356	441



Scheme 3. Mechanism of the degradation of poly(amide urethane)s **5a–d** and **10a–d**.

In the contrary to these results the poly(amide urethane)s **10a–d** show different behaviors: polymers containing 2-amino-1-ethanol and 3-amino-1-propanol in the repeating units show a clear two step decomposition. The explanation

for this result is that cyclic urethanes are eliminated first while polyamide 6 is formed which then decomposes at higher temperature (Scheme 3, route IIb). Poly(amide urethane) **10d** decomposes in one step by random chain

Table 6  
Thermal characteristics of poly(amide urethane)s **5a–d** and **10a–d**

Name	$\bar{M}_n$ GPC	First heating		Cooling		Second heating	
		$T_m$ (°C)	$\Delta H_m$ (J/g)	$T_c$ (°C)	$\Delta H_c$ (J/g)	$T_m$ (°C)	$\Delta H_m$ (J/g)
<b>5a</b>	7900	205.1	54.16	152.5	−38.47	188.5	40.88
<b>5b</b>	7700	159.0	60.04	85.3	−50.50	157.3	58.20
<b>5c</b>	6900	201.8	70.53	170.8	−69.46	185.8, 200.7	70.32
<b>5d</b>	5700	142.2, 150.7	70.72	107.2	−53.12	148.2	60.79
<b>10a</b>	8900	173.6	54.39	126.4	−34.63	172.2	36.94
<b>10b</b>	7400	154.1	80.29	81.4	−35.88	153.7	41.82
<b>10c</b>	8300	199.9	71.6	154.0	−56.24	172.1, 189.4	58.47
<b>10d</b>	11,500	162.5	77.21	121.4	−63.73	160.7	64.70



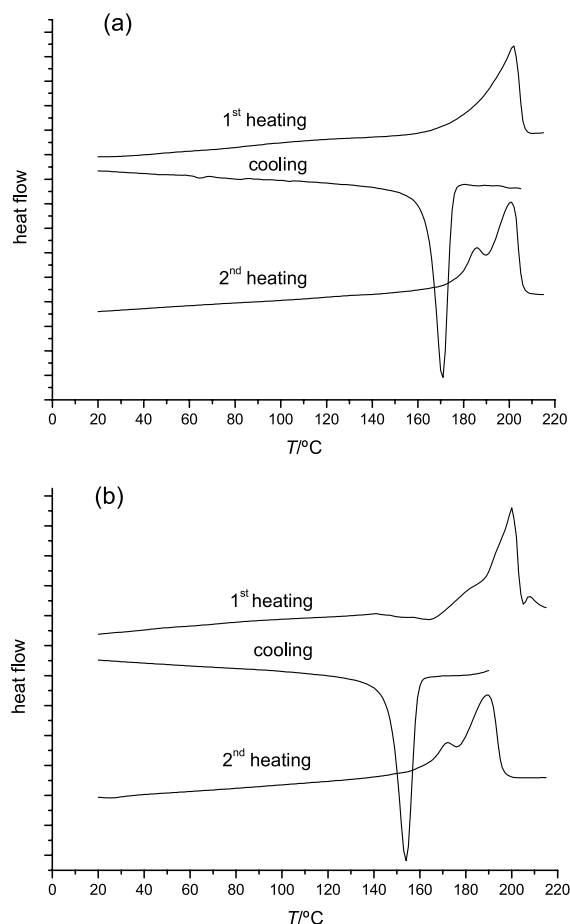


Fig. 3. DSC traces of poly(amide urethane)s; (a) **5c**, (b) **10c**.

cleavage without the formation of cyclic products (Scheme 3, route III). [8]

The TGA results obtained for the poly(amide urethane)s **5a–d** and **10a–d** clearly show three alternative routes to

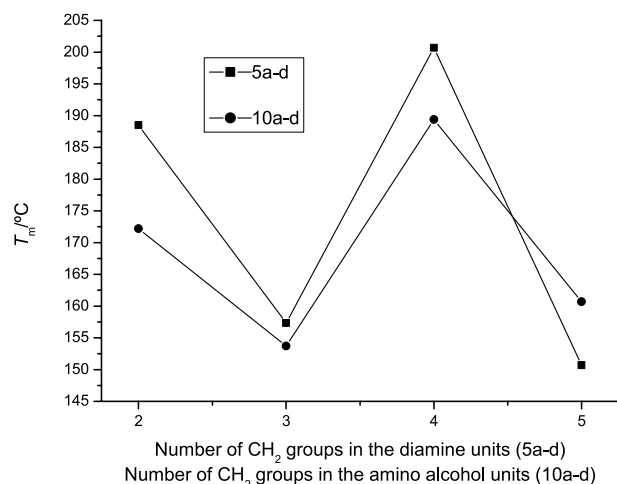


Fig. 4. Melting points of polymers (second heating); (■) poly(amide urethane)s **5a–d** obtained via polycondensation of **4a–d** in bulk at 120 °C; (●) poly(amide urethane)s **10a–d** obtained via polycondensation of **9a–d** in bulk at 120 °C.

volatile products (Scheme 3). Route I: one step decomposition is observed if both building blocks form volatile products at the same time. Route II: two step decompositions are observed when only one of the building blocks shows a highly negative free energy of formation of a ring, e.g.  $\epsilon$ -caprolactone in route IIa and cyclic 5, 6 and 7 membered urethanes for route IIb. Route III: Cyclics of both building blocks show low probability of formation; in this case no cycles are observed, instead statistical chain cleavage leads to volatile products.

A comparison of a 5, 10, 50, and 90% weight loss of the polymers as a function of temperature shows no significant difference between the two series of polymers.

According to Table 5, the temperatures at which 5, 10, 50 and 90% weight loss is observed increases with increasing number of methylene groups in both series of poly(amide urethane)s **5a–d** and **10a–d** (with one exception: 90% weight loss for **10a–d**).

DSC analysis reveals that both series of poly(amide urethane)s **5a–d** and **10a–d** are semicrystalline polymers. Characteristic DSC plots (Fig. 3) show upon first heating of polymer **5c** and **10c** only one endothermic peak at  $T_m = 201.8$  °C for **5c**, and  $T_m = 199.9$  °C for **10c** and upon second heating two endothermic peaks ( $T_m = 185.8$  and  $200.7$  °C for **5c**, and  $T_m = 172.1$  and  $189.4$  °C for **10c**). The two endothermic peaks probably are the result of different crystallite sizes. It should be mentioned that the DSC traces of polymer **10c** reveal a small crystallization peak before melting upon first heating. On cooling a narrow crystallization peak is observed at relative high temperatures which is indicative for a high degree of crystallinity of this class of polymers.

Table 6 summarizes the DSC data obtained for poly(amide urethane)s **5a–d** and **10a–d**; the differences in melting temperature and enthalpy between the two series of polymers are small. A comparison of the melting points and the melting enthalpies of the first and the second heating in most of the cases reveals slightly lower melting points and lower enthalpies in the second heating.

The melting temperature of both series shows that the poly(amide urethane)s **5a–d** and **10a–d** with an even number of carbon atoms in the diamines and amino alcohol units, respectively, have a higher melting point than those with an odd number of carbon atoms: a pronounced even–odd effect is observed (Fig. 4). This observation was made earlier for  $[n]$ -polyamides [16],  $[n]$ -polyurethanes [13,17], and poly(ester amide)s [18].

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